127. *Some Physical Properties of the Hydrides of Selenium and Tellurium.*

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CERTAIN of the physical properties of the hydrides of selenium and tellurium do not appear to have been measured, and the values for others are in evident need of amendment. In particular, data for the surface tensions, to which considerable interest attaches since the parachors of the elements have been deduced exclusively from carbon compounds, were lacking but have now been provided. Former determinations of density consisted in isolated data at one temperature, Forcrand and Fonzes-Diacon (*Ann. Chim. Phys.*, 1902, **26**, 265) giving *d* 2·57 for hydrogen telluride at —20° and *d* 2·12 for hydrogen selenide at its b. p. (—42°), and Bruylants (*Bull. Acad. roy. Belg.*, 1920, **6**, 472) giving $d^{0°}$ 2·65 for the former. A re-examination of this property was desirable, particularly in order to obtain data for the coefficients of expansion of both hydrides, since the first two workers state this to be negligible for hydrogen telluride between —30° and —10°. Also, the m. p. and b. p. of the two hydrides have been re-determined.

By utilising the experimental results now obtained, certain physical properties of the hydrides of this group are compared (see p. 978).

EXPERIMENTAL.

The hydrides of selenium and tellurium were prepared by the action of dilute hydrochloric acid on aluminium selenide and telluride, formed by direct combination of the two elements (Dennis and Anderson, *J. Amer. Chem. Soc.*, 1914, **36**, 882), the apparatus used being similar in general form to that employed by Moser and Ertl (*Z. anorg. Chem.*, 1921, **118**, 269). The telluride was prepared from tellurium which had been separated from the traces of selenium which it contained by the method described by the latter authors, except that in the final stage it was not distilled, but kept molten for some time in a stream of hydrogen.

Hydrogen, prepared from arsenic-free zinc, and freed from oxygen by passing over heated platinised asbestos, was passed through the apparatus for 2 hours before the reaction was commenced, and was subsequently employed to carry forward the resulting hydride.

The gases evolved were passed over calcium chloride and phosphoric oxide before being condensed in a vessel cooled by liquid air, the outlet from which was protected against diffusion of atmospheric moisture by a guard tube of phosphoric oxide. 80 G. of aluminium telluride yielded about 2 c.c. of liquid hydrogen telluride, and 60 g. of the selenide about 20 c.c. of liquid hydrogen selenide in about 3 hours. The solid hydrides were sealed off in the condensing vessels in an atmosphere of hydrogen, and preserved at the temperature of liquid air until required. By breaking the sealed tip of the vessel in pressure tubing, the contents were transferred, *via* a drying tube of phosphoric oxide, to a train carrying surface-tension and density vessels connected to the pump. After complete evacuation of the system, the hydride being cooled in liquid air, the solid was allowed to melt under its own pressure, and the system re-evacuated in order to remove adsorbed hydrogen. (The heat of vaporisation of these hydrides is so great that the liquid at once solidifies if the vapour be removed either by pumping or by cooling any part of the system with liquid air.) A head fraction was then removed, and the middle fraction distilled into the surface-tension and liquid density apparatus.

The telluride crystallises as a perfectly white snow-like solid which melts to a colourless liquid. The coloration mentioned by previous workers was not observed below —20°, but above this temperature the liquid became faintly yellow. The material up to that time had been exposed to daylight which had passed through four layers of glass and 4 cm. of methylated spirit.

The selenide under identical conditions shows no visible coloration at 0°.

Liquid Density.—The vessel used consisted of a thick-walled bulb connected to a capillary tube. After being filled to an appropriate point with liquid, the vessel was sealed off from the train under a vacuum. The heights of the liquid, relative to a datum line on the stem, were measured by means of a cathetometer reading to 0·02 mm. at a series of known temperatures. The vessel and contents were then weighed, the sealed tip of the capillary tube broken (care being taken to avoid loss of glass), and the hydride allowed to escape. After being cleaned and dried, the glass was weighed, and subsequently the volume of the bulb and calibration of the stem were ascertained by filling with various quantities of water, measuring the heights in the tube at a known temperature, and weighing.

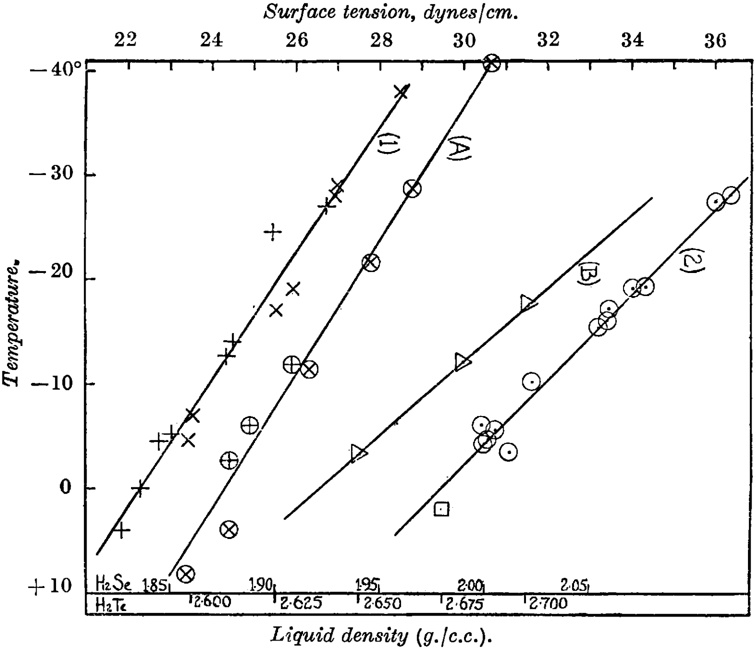
The rapid decomposition of the tellurium hydride above 0° made it imperative to determine both its liquid density and its surface tension, substantially below this temperature. With selenium hydride, the considerable vapour pressure at 0° made a similar precaution advisable. For this purpose, a bath of cooled methylated spirit, contained in a clear-walled cylindrical Dewar vessel of 1½ litres capacity, 30 cm. high and 11 cm. external diameter, was used. This bath was constantly stirred, the rate of increase in temperature being approximately 1° in 5 mins. at —40°, and much slower at higher temperatures. Readings were taken in various positions to minimise the possible effect of irregularities in the glass walls.

Table I gives the densities of the liquid hydrides over the range of temperature considered, and the results are plotted in Fig. 1. The mean density of the selenide is 1·961 g./c.c. at —27°, and the coefficient of expansion 0·00167 between this temperature and 0°;

the corresponding values for the telluride are 2·701 g./c.c. at —17·7°, and 0·00136 between —17·7° and —3·3°.

FIG. 1.

Hydrogen selenide (*curve* 1), *specimen* (1) . . . ×
" " " " (2) . . . +
Hydrogen telluride (*curve* 2), *specimen* (1) . . . ⊙
" " " " (2) . . . ⊡



Hydrogen selenide (*curve* A), *specimen* (1) . . . ⊕
" " " " (2) . . . ⊗
Hydrogen telluride (*curve* B) . . . △

TABLE I.

Hydrogen telluride.

Temp.	Vol. (c.c.), corr.	Mass (g.).	*d* (g./c.c.).
—17·7°	0·3055	0·8253	2·701
—12·1	0·3079	0·8253	2·681
— 3·3	0·3115	0·8253	2·649

Hydrogen selenide (specimen 1).

Temp.	Vol. (c.c.), corr.	Mass (g.).	*d* (g./c.c.).
—11·8	0·4779	0·9118	1·908
— 6·0	0·4829	0·9118	1·888
— 2·7	0·4858	0·9118	1·878

Hydrogen selenide (specimen 2).

Temp.	Vol. (c.c.), corr.	Mass (g.).	*d* (g./c.c.).
—41·0°	0·3562	0·7130	2·003
—28·7	0·3626	0·7130	1·966
—21·6	0·3663	0·7130	1·946
—11·4	0·3720	0·7130	1·917
+ 4·0	0·3801	0·7130	1·878
+ 8·2	0·3837	0·7130	1·858

Surface Tension.—The method of capillary rise was employed for the determination of surface tension, two tubes (D and F; data given by Mills and Robinson, J., 1927, 1823) being used. These were supported in the usual form of vessel, which, after being filled with a suitable quantity of liquid was sealed off under a vacuum. The difference in level in the two capillaries was measured by means of the cathetometer already mentioned, the vessel being tilted before each set of measurements in order that they might be made on a falling meniscus. The surface tension γ is given by $\gamma = r_1r_2g(3h + r_2 - r_1)(D - d)/6(r_1 - r_2)$, d, the density of the vapour over the liquid, being calculated from the vapour-pressure curves of Stein (J., 1931, 2134).

The results (Table II) give a mean value for γ for hydrogen selenide of 26·74 ± 0·05 dynes/cm. at —27°, with a temperature coefficient of 0·165 dyne/cm. between —27° and 0°. The mean surface tension of the telluride is 36·35 ± 0·05 dynes/cm. at —28°, with a coefficient of 0·246 dyne/cm. between —28° and —4·6°.

TABLE II.

Hydrogen selenide.			*Hydrogen telluride.*		
Spec.	Temp.	γ, dynes per cm.	Spec.	Temp.	γ, dynes per cm.
1	—38·0°	28·49	1	—28°	36·35
1	—29·0	27·00	1	—27·4	36·00
1	—28·0	26·96	1	—19·3	34·34
1	—19·0	25·93	1	—19·2	34·02
1	—17·0	25·54	1	—17·2	33·48
1	— 7·0	23·55	1	—16·0	33·44
1	— 4·6	23·43	1	—15·4	33·22
2	—27·0	26·74	1	—10·2	31·62
2	—24·5	25·42	1	— 6·0	30·45
2	—14·0	24·51	1	— 5·6	30·74
2	—12·6	24·32	1	— 4·6	30·59
2	— 5·2	23·02	1	— 4·2	30·50
2	— 4·5	22·77	1	— 3·5	31·12
2	+ 0·0	22·29	2	+ 2·0	29·49
2	+ 4·0	21·86			

Melting Point of Hydrogen Telluride.—Ernyei (*Z. anorg. Chem.*, 1900, **25**, 313) and Forcrand and Fonzes-Diacon (*loc. cit.*) have given the values —54° and —48° respectively. In the present work the vessel shown in Fig. 2 was used, the thermocouple being inserted in the sealed-in thin glass sheath. After being filled from the vacuum train with about 4 g. of material, the vessel was sealed off at *A*. Three values of the arrest given on the heating curve were —51·0°, —50·6°, and —51·7°. The variation is ascribed to the low thermal conductivity of the hydride. The mean value, —51·2°, is believed to be within ± 1° of the truth.

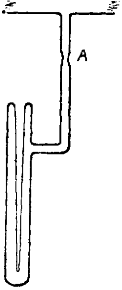
Boiling Point of Hydrogen Telluride.—This has been previously given as —1·8° (Bruylants), above 0° (Ernyei), 0° (Forcrand and Fonzes-Diacon), + 0·5° (Dennis and Anderson). A similar vessel to that described for the determination of the melting point was used, the liquid being allowed to boil at atmospheric pressure into an atmosphere of dry hydrogen. The decomposition of the material is rapid at this temperature, and this may account for the fact (also observed by Dennis and Anderson) that the b. p. is not sharp. That of the middle fraction of one specimen was —5·1°/774 mm., at which point the temperature remained within + 0·02° for 5 minutes; with material from a different preparation, —3·9°/752 mm. Evidently the b. p. is lower than that previously reported, being about —4° to —5°.

The thermocouple used in these measurements was that already calibrated for a previous investigation (Pearson and Robinson, this vol., p. 652).

Discussion of Results.

The experimental results allow the parachors of hydrogen telluride and hydrogen selenide to be calculated, with the following results: H_2Te, 115·7 at —28°, 115·2 at —4·6°; H_2Se, 94·5 at —27°, 94·8 at 0°. Assuming covalent binding, and subtracting 34·2 for the parachor of the two hydrogen atoms, we obtain parachors of 81·5 and 81·0 for tellurium, and 60·3 and 60·6 for selenium at the respective temperatures. The mean values for the two elements when present in compounds containing carbon are 79·4 (Burstall and Sugden, J., 1930, 230) and 62·5 (Henley and Sugden, J., 1929, 1058) respectively, with which the present results are in satisfactory agreement. Incidentally, the parachor of sulphur in hydrogen sulphide, as calculated from the surface-tension and density determinations of McIntosh and Steele (*Z. physikal. Chem.*, 1906, **55**, 136), which do not appear to have been used previously, is 47·76 at —84° and 47·45 at —62·2°, results which are again in close agreement with the accepted value for the element, *viz.*, 48·2.

FIG. 2.



The values for the Eötvös–Ramsay–Shields constants, given with certain other physical properties of the group in Table III, indicate that hydrogen sulphide is slightly associated, but that the telluride and selenide are normal liquids, presenting a marked contrast to water, for which the value is 1·4 and the temperature coefficient is considerable.

An interesting point has arisen from an examination of the values of the surface tensions at the respective b. p.'s. These are very nearly identical in the case of the hydrides of sulphur, selenium, and tellurium (mean value 29·2 dynes/cm.), whereas that of water at the b. p., where it consists largely of dihydrol molecules, is about twice this figure, *viz.*, 59.

For analogous compounds of the same family of elements, if the period numbers of the elements are plotted against (1) the surface

TABLE III.

	H_2O.	H_2S.	H_2Se.	H_2Te.
Critical temp.	366°	100·4°	137°	200° (calc.)
B. p.	100°	−60·5°	−41·5°	−4° to ±1°
M. p.	0°	−83°	−66°	−51°
Liquid density at b. p.	0·958	0·967	2·004	2·650
Coeff. of expansion $\times 10^5$	70 (80—100°)	174 (−84° to −62°)	167 (−27° to −0°)	136 (−18° to −3°)
γ at b. p.	58·9	28·7	28·9	30·0
$d\gamma/dt$	0·168 (0° to 100°)	0·213 (−84° to −62°)	0·165 (−27° to −0°)	0·246 (−28° to −4·6°)
K (Eötvös–Ramsay–Shields)	1·42 (0°) 1·51 (80°)	1·90 (−84°) 1·91 (−62°)	1·96 (−27°) 2·03 (0°)	2·01 (−28°) 2·00 (−4·6°)
Trouton's constant	25·9	21·8	20·4	16·7
Molecular parachor	53·1 (0°) 52·1 (100°)	82·0 (−84°) 81·7 (−62°)	94·5 (−27°) 94·8 (0°)	115·7 (−28°) 115·2 (−4·6°)
Mean parachor of element	18·3	47·6	60·5	81·3

tensions, at the respective b. p.'s, and (2) the boiling points, the forms of the two curves are similar, so that when the boiling points lie on a straight line the surface tensions also show a linear relationship. When there is an anomaly in the boiling point, brought about by association of the liquid, a corresponding inflexion occurs in the plot of surface tensions. In the hydrides and carbonyls of the oxygen family, for instance, straight lines are given by the boiling points and the surface tensions (extrapolated in all cases to the b. p.) of the latter (COSe, Pearson and Robinson, this vol., p. 652; COS, Pearson, Robinson, and Trotter, *ibid.*, p. 660; CO_2, Verschaffelt, "International Critical Tables"), whereas the lines for the hydrides are slightly inflected at hydrogen sulphide but radically changed in direction to the point for the highly associated water molecule (see Fig. 3).*

Examination of available data in other compounds, some of greater complexity, appears to indicate that a similar rule obtains. The hydrides of the nitrogen family are of interest, for here a considerable fall is observed in the surface tensions from liquid ammonia to liquid phosphine. Unfortunately, however, the absence of surface-tension data for arsine and stibine does not allow of a full comparison being made, but the melting-point curve (Paneth and Rabinowitsch, *Ber.*, 1925, **58**, 1147) suggests that a similar relationship would be found, particularly as Trouton's constant indicates some association for ammonia.

Further work will probably show that this is a generalisation of

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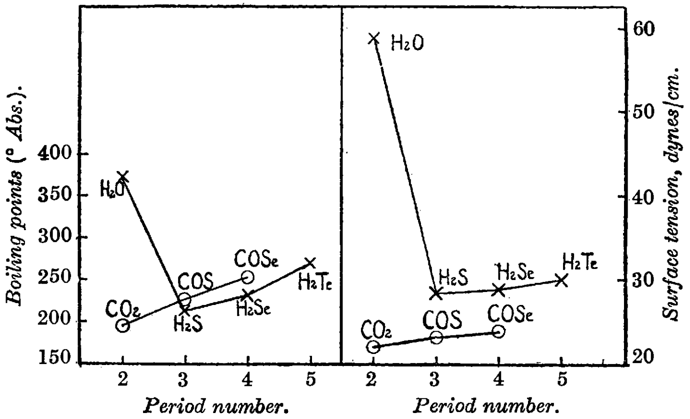
* The surface tensions under consideration were measured at different pressures, but the alteration with pressure is insignificant (compare Lynde, *Physical Rev.*, 1906, **22**, 181).

fairly wide application and a method of detecting association. Moreover, this analogy between boiling point and surface tension at the boiling point allows Paneth and Rabinowitsch's extrapolatory method (*loc. cit.*) of estimating the b. p.'s and m. p.'s of compounds of the sixth, seventh, and eighth periods to be extended to the surface tensions.

FIG. 3.



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